PREPARATION, CHARACTERIZATION AND ANTIMICROBIAL PROPERTIES OF CHITIN BASED POLYVINYL ALCOHOL BLENDED FILMS

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Abstract

In this research, high strength chitin (CT) - based polyvinyl alcohol (PVA) blended films were prepared by adding different amounts of PVA to chitin dissolved in an aqueous formic acid solution and then by a solvent evaporating technique at room temperature. All prepared blended films have smooth surfaces, are highly transparent, and pale yellow in colour. The physical parameters, the mechanical properties, the degree of swelling and water uptake the prepared blended films were determined. The swelling and water uptake of the blended membrane have a higher degree of hydration, as measured by swelling and water uptake, which can be altered by varying the weight percent of PVA in the membrane matrix. From FT IR analysis, the characteristic absorption peaks of the CT-based PVA blended film clearly showed that the two polymers were blended. A SEM micrograph of CT-based PVA blended films showed homogeneous and amorphous phases. The XRD patterns of the CT-based PVA blended films also exhibited crystallinity. According to TG-DTA analysis, the thermal stability of the CT-based PVA blended were found to decrease. All of the prepared CT-based PVA blended films showed effective antimicrobial activities. The prepared CT-based PVA blended films exhibited excellent biocompatibility and safety in the environment and may also be intended for use in burning dressings and packaging materials.

Keywords: Chitin, polyvinyl alcohol, mechanical properties, antimicrobial activity

Introduction

Because of the ever-increasing production of polymers, which causes environmental pollution, the current problem of polymer utilization is becoming more and more pressing. This problem can be solved by developing biodegradable polymer materials that decompose under environmental conditions to produce harmless byproducts. The most efficient and economically profitable research trend in this field appears to be the production of polymer materials by combining synthetic and natural, biodegradable materials (Rogovina *et al*., 2011). Biopolymers such as cellulose, chitin, and chitosan are abundant. They are primarily obtained from the exoskeletons of crustaceans such as shrimp, but they can also be obtained from fungi and some insect wings. It is widely known. Poly (vinyl alcohol) (PVA) is a nontoxic, water-soluble synthetic polymer with good film-forming ability due to its large number of hydroxyl groups, which allows it to react with a wide range of functional groups (Hefian *et al*., 2010). Polymer blending is a useful method for creating new materials with desired properties, and there has been significant scientific and commercial progress in the field of polymer blends (Cascone, 1997; Fukae *et al*., 1990).

In this paper, chitin/PVA blend films were created by solution-casting chitin and PVA solutions in concentrated formic acid at various compositional ratios. The physical properties, thermal properties, mechanical properties, morphology, and swelling behaviour of blended compositions were investigated.

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Materials and Methods

Chitin and Polyvinyl alcohol (Molecular weight 20, 000, degree of hydrolysis 98%) were purchased from the British Drug House (BDH) Chemical Ltd., England. All other chemicals used were of analytical reagent grade. In all investigations, the recommended standard methods and techniques involving both conventional and modern methods were provided.

Preparation of Chitin-Polyvinyl Alcohol (CT-PVA) Blended Films

Chitin solution 2 % w/v was prepared by dissolving 2 g of chitin (CT) in 100 ml of 90 % v/v formic acid with frequent stirring for 30 minutes at room temperature to get a clear solution. The five different amounts of PVA samples (2 g, 4 g, 6 g, 8 g, and 10 g) were added to each beaker containing 100 ml of 2% chitin solution by thoroughly stirring the mixed polymer for about 30 minutes to obtain a series of CT-PVA blends. The blended polymer solutions were kept for sufficient time to remove any bubble formation and were cast onto a cleaned and dried melamine plate at room temperature. The melamine plates containing the blend solution were left for about 3 days to obtain CT-PVA blended films. After drying, the membranes were easily removed from the melamine plates and immersed in a 1 M NaOH solution to remove residual materials. They were then washed with distilled water to remove alkali and unreacted materials, and finally dried at room temperature. The prepared sample was coded as CT-PVA2 for 2 g of PVA, CT-PVA4 for 4 g of PVA, CT-PVA6 for 6 g of PVA, CT-PVA8 for 8 g of PVA, and CT-PVA10 for 10 g of PVA, respectively.

Physical Parameter Measurement of CT-PVA Blended Solution

The details of the measurement of the physical parameters such as pH, specific gravity and viscosity of the different CT-PVA solutions have been reported earlier (Aung Than Htwe *et al.*, 2021).

Determination of Mechanical Properties

The details of the measurement of tensile strength, elongation at break and tear strength of the samples have been described earlier (Aung Than Htwe *et al.*, 2021). The tensile strength (TS), elongation at break (EB), and tear strength of films were determined using the UCT-5T model (UTM (Orientec Co. Ltd.)). The sample sheets were cut using an ASTM D638 M-III dumbbell cutter. The test conditions were 27 °C temperature, 65 % humidity in the test chamber, 1 mm/min tensile velocity, and 10% load cell scale of 50 N. The sample thickness was measured in three positions, namely, the top, middle, and bottom of the membrane. The thickness value was averaged according to the thickness of the sample. The formula of the TS used as shown in Eq. (1):

$$TS = \frac{F_{max}}{A} \tag{1}$$

where TS is tensile strength (MPa); F_{max} is the force of TS (N); and A is sample surface area (mm^2) (Hidayati *et al.*, 2021).

The elongation at break was calculated by dividing the deformation at the moment of rupture by the initial length of the sample, according to equation (2).

$$R = \frac{L}{C_i} \times 100 \tag{2}$$

where R is elongation at rupture expressed in %; L is distance at moment of rupture expressed in mm; and C_i is initial sample length in mm (Goncalves *et al.*, 2019).

Determination of Water Uptake (%)

The water uptake (%) of the as-prepared films was determined by measuring the weight of the films after immersion in distilled water for 0–60 min in comparison with the dry weight of the films before the immersion. The water uptake (%) was calculated according to the following relationship:

$$\text{Water uptake (\%)} = [W_s\text{-}W_d/W_d] \times 100 \text{ \%,} \tag{3}$$

where W_s and W_d represent the weight of the films after and before immersion. It is important to note that all the experiments were carried out at room temperature.

Determination of Degree of Swelling

The swelling behaviour of the as-prepared films was studied by measuring the weight of the films after immersion in distilled water for 0–60 min in comparison with the dry weight of the films before the immersion. The degree of swelling was calculated according to the following relationship:

$$\text{Degree of swelling (\%)} = [W_s\text{-}W_d /W_s] \times 100 \text{ \%,} \tag{4}$$

where W_s and W_d represent the weight of the films after and before to immersion. It is important to note that all the experiments were carried at room temperature.

Characterization

The prepared blend films were analysed by FTIR in a wide range of wavelengths between 400 cm^{-1} and 4000 cm^{-1} with a resolution of 1 cm^{-1} and 3 scans/sample. A Perkin Elmer GX System FT-IR spectrophotometer was used. A SEM study of the prepared blend films was carried out by JSM–5610 LV. Scanning Electron Microscope, JEOL at 20 kV. The dried sample film was cut and was sputter coated with platinum using a microscope sputter coater and viewed through the microscope. An X-ray powder diffractometer (XRD) was used to perform X-ray diffraction studies with Ni filtered Cu Kα X-ray radiation. Thermo gravimetric analysis was carried out in a nitrogen atmosphere at a heating rate of 20.0 kJmin^{-1} and scanning from 40 ºC to 600 ºC. Thermogravimetric analysis was carried out in a nitrogen atmosphere at a heating rate of 15 °C/min up to a temperature range of 1400 °C on the DTG-60H thermal analyzer.

Determination of Antimicrobial Test

The different chitin based PVA blended films were tested with *Bacillus subtilis, Staphylococcus aureus, Pseudomonus aeruginosa, Bacillus pumilus, Candida albicans* and *E. coli* species to investigate the nature of antimicrobial activity. The details procedure of the antimicrobial test has been reported earlier (Aung Than Htwe *et al*., 2021).

Results and Discussion

Physical Properties of CT- Based PVA Solution

Figure 1 indicates the physical parameters of CT- based different amounts of PVA blended solutions. The measuring parameters are pH, specific gravity and viscosity. From the value of pH of CT-based different amount of PVA blended solutions are slightly acidic and distilled water in the range of 4 to 5. The specific gravity is 1.163 in CT-PVA2, 1.345 in CT-PVA4, 1.348 in CT-PVA6, 1.374 in CT-PVA8 and 1.282 in CT-PVA10, respectively. It can be seen that increasing the PVA content, Causes a slight increase in the specific gravity. The viscosity value is 6.86 cPs in CT-PVA2, 14.45 cPs in CT-PVA4, 34.93 cPs in CT-PVA6, 69.45 cPs in CT-PVA8 and 150.6 cPs

in CT-PVA10. It is observed that the higher the PVA content, the higher the viscosity. Thus, all physical parameters of CT-PVA blended solutions showed obviously significant values.
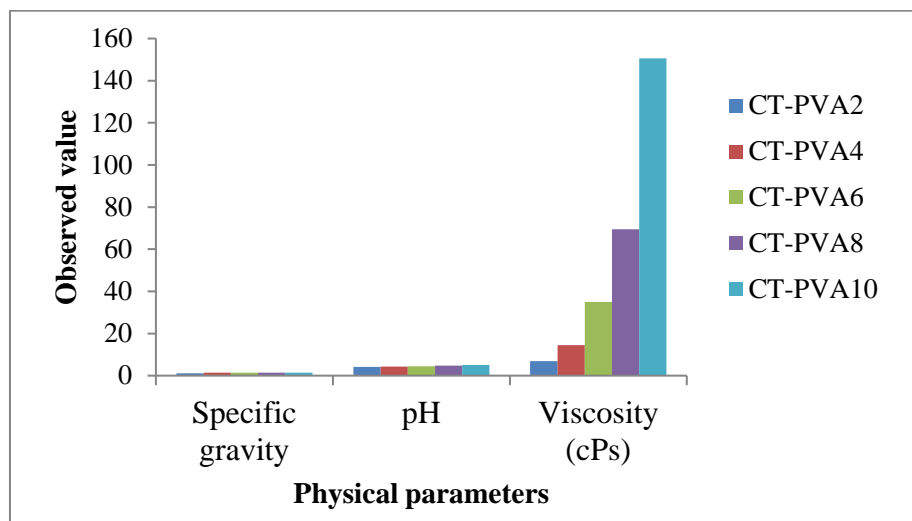
Figure 1. The physical parameter of the chitin based polyvinyl alcohol blended solutions

**Mechanical Properties of CT- Based PVA Films**

　　　The mechanical properties in terms of tensile strength, elongation at break (%), tear strength are important parameters which reveal the nature of films. The mechanical properties of CT based PVA blended films are presented in Figure 2. The thickness values of CT- based PVA blended films were 0.12 mm in CT-PVA2, 0.27 mm in CT-PVA4, 0.40 mm in CT-PVA6, 0.50 mm in CT-PVA8 and 0.70 mm in CT-PVA10. It was found that as the amount of PVA content increased, the thickness also increased. The tensile strength values of CT- based PVA blended films were 4.4 MPa in CT-PVA2, 2.7 MPa in CT-PVA4, 2.3 MPa in CT-PVA6, 1.7 MPa in CT-PVA8 and 1.2 MPa in CT-PVA10, respectively. Tensile strength of CT based PVA blended films decreased from 4.4 MPa to 1.2 MPa. The percent elongation at break was 205 % in CT-PVA2 content, however, it was significantly increased to 444 % in CT-PVA4 and then to 529 % in CT-PVA6. As seen in Figure 2, the tensile strength and % elongation values are flexible in CT-PVA6. The tear strength is another mechanical property of the nature of films. It indicated that the tear strength of CT- based PVA blended films significantly decreased from 34.7 kN/m in CT-PVA2 to 11.0 kN/m in CT-PVA8. It can be concluded that according to the mechanical properties such as tensile strength, percent elongation at break, tear strength, and thickness, among CT based PVA blended films, CT-PVA6 has the highest value of mechanical properties.
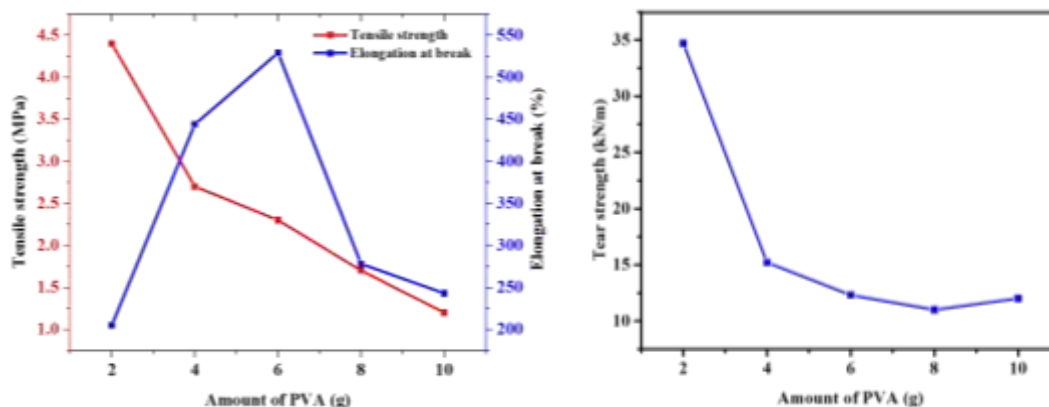
Figure 2. The mechanical properties of chitin based PVA blended films

Degree of Swelling (%) Behaviour

The degree of swelling of CT-based PVA blended films are shown in Figure 3 as a function of immersion time in distilled water at room temperature. As shown in figure, with increasing PVA content, the ultimate degree of swelling before 50 min of immersion time of CT-PVA blend films were found to increase from ca. 75.3 to ca. 84.6 %, when PVA content increased from 2 g to 8 g. After 50 min, all of the blended films were found in deswelling nature. The maximum value for the degree of swelling of CT-PVA6 blended film has 84.6 % at 50 min. The fact is attributed to a more rigid network formed by the inter-intra polymer chain reactions that have occurred, reducing the flexibility and number of hydrophilic groups of hydrogel which is unfavourable to the swelling rate. So, these results correspond to the hydrogel mechanism. The PVA chains are physically entangled with the chitin chains, forming a hydrogel network (Özturk, 2011).
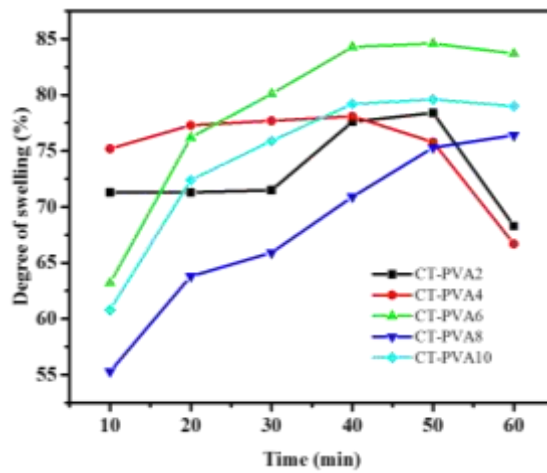
Figure 3. The degree of swelling of chitin based PVA blended films

Water Uptake (%)

The degree of water uptake was investigated with increasing immersion time. The water uptake as a function of time for CT-PVA hydrogel film is shown in Figure 4. As seen in the figure, the water uptake of CT-PVA blended film was significantly different according to the amount of PVA content. The water uptake was the amount of water entrapped in the matrix, including bound water. CT-PVA6 had the highest degree of water uptake content (550.9 %) at 50 min. The water uptake may impart stickness and durability.
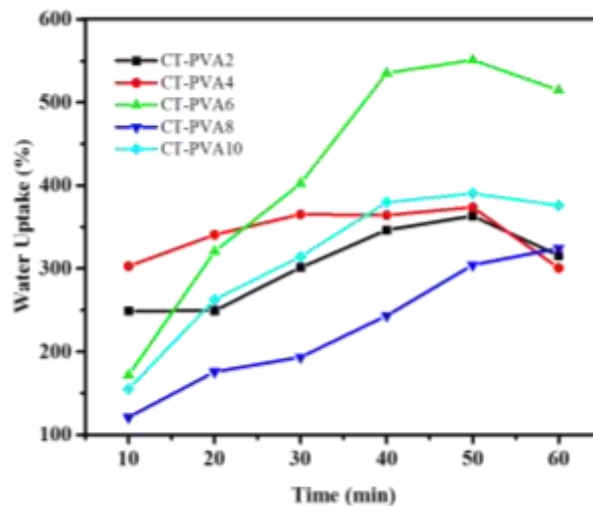

Figure 4. The water uptake (%) of chitin-based PVA blended films

Characterization

FT IR analysis

The FTIR spectra of chitin-based PVA films are presented in Figures 5 and Table 1. As can be seen, the increase in the PVA concentration in the blended films caused a decrease in the intensity of the band arising from NH bending (amide II) at 1416 cm^{-1} of chitin. Also, an increase in the intensity of CH group at around 2939 cm^{-1} was found as the PVA content increased. As seen in figures, all of the blended films are agreement with the range of absorption peak to the references peak range.
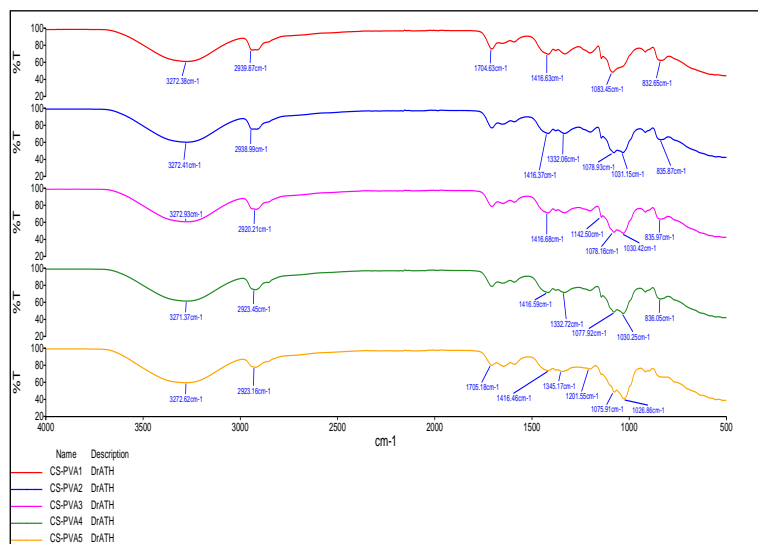
**Figure 5.** FTIR spectra of chitin-based PVA blended films

Table 1. FT IR Characteristic Bands of Chitin based PVA Blended Films

Samples	C-C & C-H bend	C-OH stretch	CH	NH amide I	C=O amide I	CH stretch	OH stretch
CT-PVA2	832.65	1083.45	1332.02	1416.63	1704.63	2939.87	3272.38
CT-PVA4	835.87	1078.93	1332.06	1416.37	1703.68	2938.99	3272.41
CT-PVA6	835.97	1078.16	1332.67	1416.68	1703.65	2920.21	3272.93
CT-PVA8	836.05	1077.92	1332.72	1416.59	1704.43	2923.45	3271.37
CT-PVA10	836.02	1075.91	1345.17	1416.46	1705.18	2923.16	3272.62

Ref: Lee *et al.*(1996), Nakamoto (1970)

SEM analysis

Morphological tests of the films were performed by using SEM technique. The SEM images for (a) CT-PVA2, (b) CT-PVA4, (c) CT-PVA6, (d) CT-PVA8 and (e) CT-PVA10 films are shown in Figure 6. It can be found that all of the blended films exhibited homogeneity showing a certain miscibility between chitin and PVA. Finally, the SEM clarifications have supported the measured mechanical and thermal properties of the biocomposite films.

    (a) CT-PVA2   (b) CT-PVA4   (c) CT-PVA6

    (d) CT-PVA8   (e) CT-PVA10
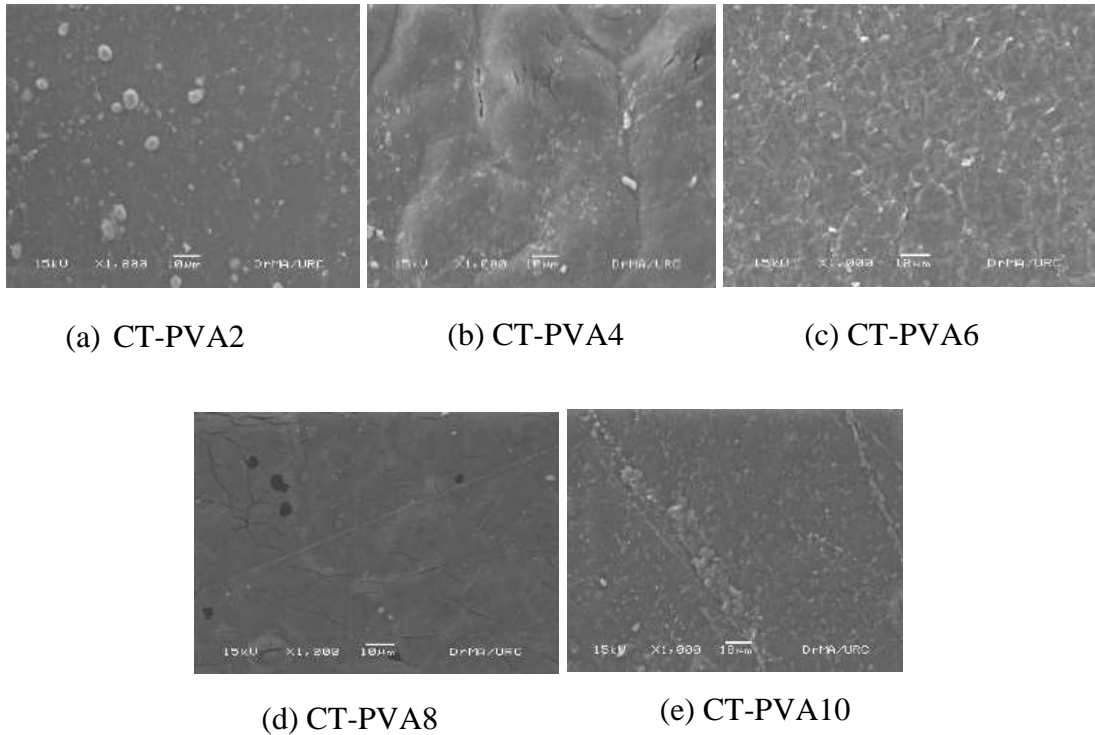
Figure 6. The SEM images of the surface of chitin-based PVA blended films

XRD analysis

X-ray diffractograms of the chitin/PVA binary blend, are shown in Figure 7. Hema, Ramya, and Sudha (2012) reported that the two characteristic crystalline peaks of pure chitin were found at $2\theta = 9.32°$ and $19.25°$, corresponding to the (010) and (020) and (110) planes, respectively. When PVA crystallized in a monoclinic unit cell, the main peaks in the XRD pattern should appear at the 2θ angles of 11.3, 19.7, 22.9, 28, 32.5, and 40.9° (Peesan, 2003). As seen in Figure 4(a) to (e), in all of the chitin-based PVA blended films, the peak of the hydrated crystalline structure of chitin at 9.32° is absent, and the strong 19.2° peak with (110) plane is diminished. It illustrates that existence of PVA decreases the crystallinity of chitin in the binary blend. Lastly, it can be deduced that the XRD patterns would be expressed as simply mixed patterns of different components in the mechanical and thermal blending cases.
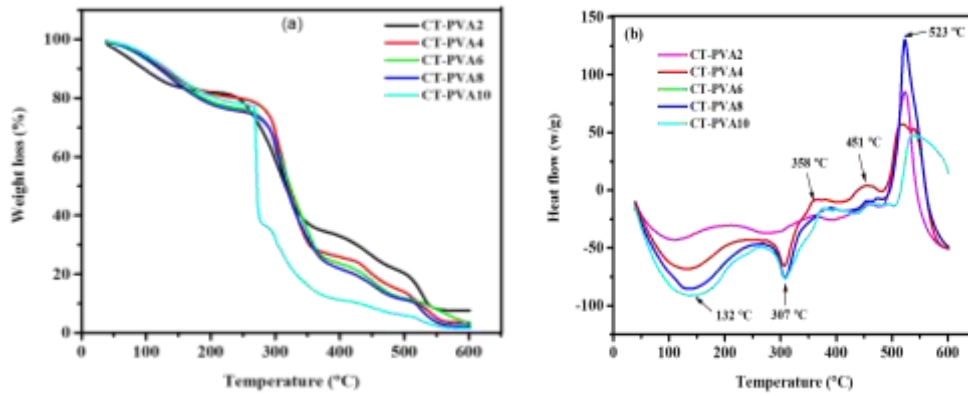
(a) CT-PVA2

(b) CT-PVA4

(c) CT-PVA6

(d) CT-PVA8

(d) CT-PVA10
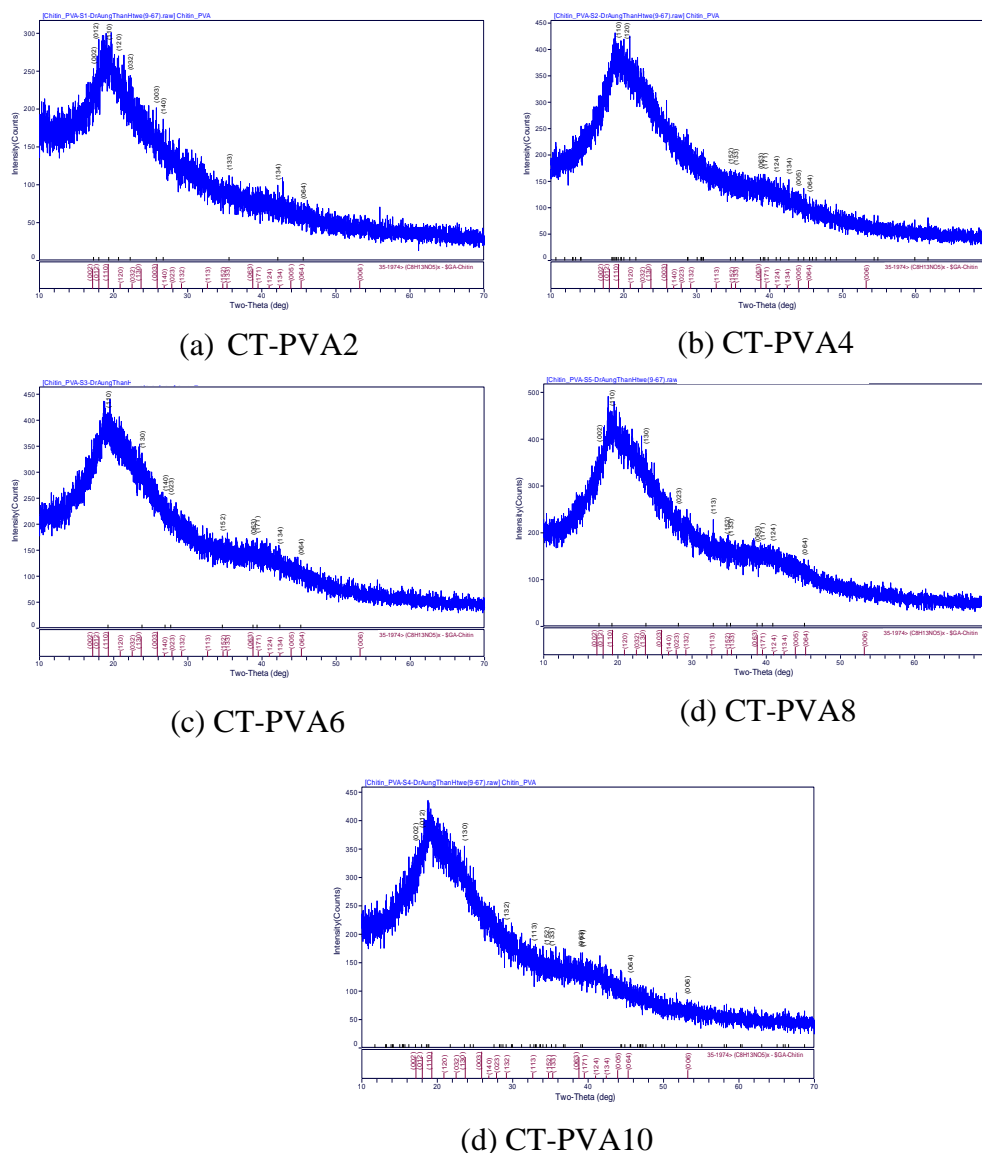
Figure 7. X-ray diffraction patterns of chitin-based PVA blended films

Thermogravimetric analysis

TGA is a useful technique to assess the thermal stability of polymers and polymers blends. The decomposition and thermal stability of chitin and blended films were determined from thermograms, as shown in Figure 8. As seen in Figure 8, the CT-PVA2, CT-PVA4, CT-PVA6, CT-PVA8 and CT-PVA10 films have weight loss in four stages. The first stage ranges from 39°C to 50°C; weight loss was 15.83% in CT-PVA2, 15.99% in CT-PVA4, 10.69% in CT-PVA6, 5.54% in CT-PVA8 and 6.53% in CT-PVA10. There is a loss of absorbed water. In the second stage, in the temperature range between 150°C to 290°C, was observed as 27.70% in CT-PVA2, 21.32% in CT-PVA4, 26.72 % in CT-PVA6, 16.64 % in CT-PVA8 and 19.59% in CT-PVA10. This is due to the evaporation of some organic materials. In the third stage, weight loss of 31.66% in CT-PVA2, 53.30% in CT-PVA4, 48.10% in CT-PVA6, 49.92% CT-PVA8 and 39.18% in CT-PVA10 was observed to take place within the temperature range of 290°C to 378°C. In this stage, weight loss is due to partial decomposition of chitin and PVA polymer. The fourth stage ranges between about the temperature range of 378°C to 600°C with 15.83% in CT-PVA2, 5.33% in CT-PVA4, 10.6 % in CT-PVA6, 24.96% in CT-PVA8 and 32.64% in CT-PVA10. There is complete degradation of chitin and PVA polymer.

Figure 8. (a) TGA curves and (b) DTA curves of chitin-based PVA blended films

Antimicrobial Activity

Antimicrobial activity of CT-PVA2, CT-PVA4, CT-PVA6, CT-PVA8 and CT-PVA10 films are shown in Figure 9 and Table 2. As seen in Figure 9 and Table 2, antimicrobial tests of all blended films were performed on the agar medium. As a result of the blended films, they all have antimicrobial activity. It can be concluded that according to the antimicrobial activity, the blended CT-PVA film may be intended for use as burn dressing and food packaging materials.

(1) CT-PVA2
(2) CT-PVA4
(3) CT-PVA6
(4) CT-PVA8
(5) CT-PVA10
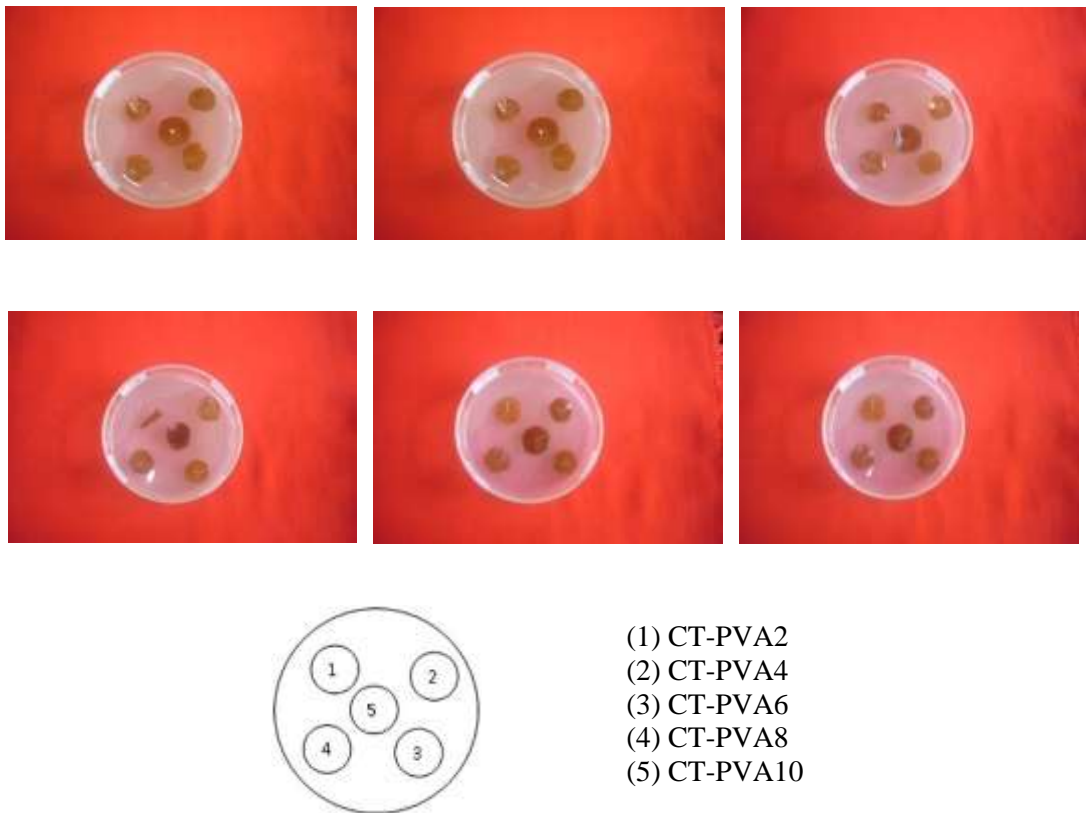
Figure 9 Antimicrobial activity of prepared chitin-based PVA blended films

Table 2 Antimicrobial Activity of CT-PVA Blended Film by Agar Disc Diffusion Method

No	Microorganism	Samples				
		CT-PVA2	CT-PVA4	CT-PVA6	CT-PVA8	CT-PVA10
1	*Bacillus subtilis*	++	++	++	+	++
2	*Staphylococcus aureus*	++	++	++	+	++
3	*Pseudomonas aeruginosa*	++	++	++	+	++
4	*Bacillus pumilus*	++	++	++	+	++
5	*Candida albicans*	++	++	++	+	++
6	*E.coli*	++	++	++	+	++

Disc diffusion (mm) $\geq 21(+++)$ susceptible, $17.20(++)$ intermediate, $\leq16(+)$ resistant

Conclusion

In this study, polymer blend membranes of chitin-based polyvinyl alcohol were prepared by blending, casting and solvent evaporating techniques. All prepared CT-based PVA blended films showed a plain, clear, smooth surface, were flexible, highly transparent, and were of a light-yellow colour. The swelling and water uptake of blend membrane has a higher degree of hydration, as measured by swelling and water uptake, which can be altered by varying the weight percent of PVA in the membrane matrix. FT IR analysis showed that there exist intermolecular interactions between CT and PVA. The SEM analysis showed that all of the blended films exhibited homogeneity showing a certain miscibility between chitin and PVA. The XRD patterns also showed a reduction of crystallinity of chitin as diffused rings in the blend, but hold amorphous nature. From TG-DTA analysis, the thermal stability of CT-based PVA blended films was found to decrease and the weight loss to increase. The properties of various types of CT-based PVA blended films were tested on their antimicrobial activities by using agar disc diffusion method. It can be noted that all of the microbial agents that come in contact with films are active. According to these results, the prepared CT-based PVA blended films could be used as burn dressing and food packaging materials.

Acknowledgements

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